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PATENT SPECIFICATION

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NO DRAWINGS

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COMPLETE SPECIFICATION

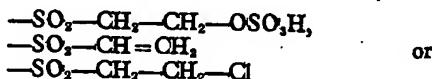
Metal-Containing Disazo Dyestuffs and process for
their manufacture

We, FARBWERKE HOECHST AKTIENGESELLSCHAFT vormals Meister Lucius & Brüning, a body corporate recognised under German Law, of 6230 Frankfurt (M)-Hoechst, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

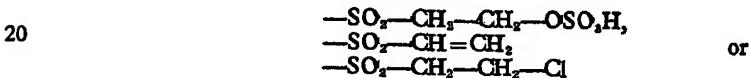
Specification No. 913,517 describes and claims complex metal compounds of azo-dyestuffs of the general formula



in which F represents an azo dyestuff molecule containing a grouping capable of forming metal complexes and also at least one nuclear bound sulphonic or carboxylic acid group, A represents a group

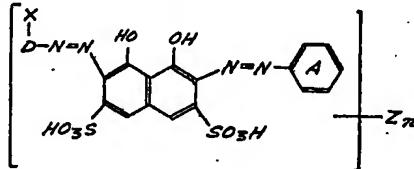


and n is the whole number 1 or 2; and a process for the manufacture of complex metal compounds of azo-dyestuffs, wherein an agent yielding metal is reacted with an azo-dyestuff containing a grouping capable of forming complex metal compounds and containing one or two of the groups:



and also at least one nuclear bound sulphonic or carboxylic acid group.

The present invention provides new metal-containing disazo dyestuffs and a process for their manufacture; more particularly, the present invention provides complex copper, cobalt or chromium compounds of disazo dyestuffs which, in the form of their free acids, correspond to the general formula

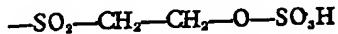


(1)

wherein D represents the radical of a diazo component of the benzene or naphthalene series, X represents a hydroxyl or carboxyl group bound in *o*-position to the azo bridge, Z represents a group of the formula

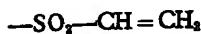
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(2)

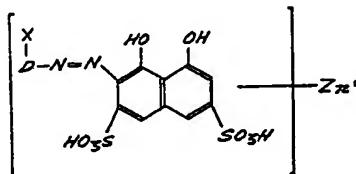
or



(3)

which is linked to the residue D and/or residue A and n represents 1 or 2, and wherein
5 the benzene nucleus A may carry substituents.

This invention is based on the observation that valuable complex copper, cobalt,
10 or chromium compounds of disazo dyestuffs, which in the form of their free acids,
correspond to the above formula (1) may be obtained by coupling complex copper,
cobalt or chromium compounds of monoazo dyestuffs, which in the form of their free
acids correspond to the general formula



(4)

wherein D, X and Z have the meanings given above and n' represents 0, 1 or 2,
15 with diazotized amines of the benzene series in a weakly alkaline, neutral or weakly
acid medium, the components being so selected that the metal-containing disazo dye-
stuffs obtained contain one or two groups of the formula Z.

The radical D and the benzene nucleus A in the above formula (1) may carry
any substituents in addition to the groups of the above formulae (2) and (3). As
examples, the following may be mentioned: halogen atoms for example chlorine
or bromine atoms, nitro, cyano, acetylamo, unsubstituted and substituted alkyl
groups, for example methyl, ethyl or trifluoromethyl groups, alkoxy groups for ex-
ample methoxy or ethoxy groups, alkylsulphone groups for example methyl- or
ethyl-sulphone groups, and water-solubilizing groups, for example sulphonic acid,
sulphonic acid amide, sulphonic acid monoalkylamide, sulphonic acid dialkylamide
or carboxylic acid groups.

The diazotization of the aminobenzenes is carried out in the usual manner at 0
to 5° C. and the diazo compounds obtained are coupled with the metallised monoazo
dyestuffs of the above formula (4) advantageously at 10° to 40° C. in a weakly
acid, neutral or weakly alkaline medium, at a pH-value from 4 to 9 and preferably
at a pH-value in the range of from 5 to 7. The complex metal disazo dyestuffs formed
are precipitated from the reaction mixture by means of sodium chloride or potassium
chloride, filtered, washed and dried. If desired, the products of the invention may
be isolated by spray-drying the dyestuff solution directly after the coupling reaction.

The diazotizable amines which may be used for preparing the metallised disazo
dyestuffs of the present invention, are preferably those containing electro-negative
groups. As examples, there may be mentioned: 1-aminobenzene-4-sulphonic acid, 1-
aminobenzene-2,4- or 2,5-disulphonic acid, 4-nitro-1-aminobenzene, 4-methylsulphonyl-
1-aminobenzene, 1-aminobenzene-4-sulphonic acid amide, 4-nitro-2-methoxy-1-amino-
1-aminobenzene, 4-vinylsulphonyl-1-aminobenzene, the sulphuric acid esters of 1-aminobenzene,
4-β-hydroxyethylsulphone, 2-aminoanisole-4-β-hydroxyethylsulphone, 1-
amino-2,5-dimethoxybenzene-4-β-hydroxyethylsulphone and 1-amino-2-methoxy-5-
methyl-4-β-hydroxyethylsulphone.

The metallised starting dyestuffs of the above formula (4) may be obtained in
known manner by coupling 1,8-dihydroxynaphthalene-3,6-disulphonic acid with di-
azotised aromatic amines of the benzene or naphthalene series which contain, a sub-
stituent capable of forming a complex metal or a substituent convertible into a
group forming a metal complex in *o*-position to the diazo group, for example, a
hydroxyl group, a carboxyl group or, as a group convertible into a hydroxyl group, a
methoxy or ethoxy group. The conversion of the methoxy or ethoxy group into the
hydroxyl group occurs during the metallization, particularly in the coppering process.

The monoazo dyestuffs thus obtained are then converted into the corresponding
complex metal compounds, whereby 1:1- or 2:1- complex metal dyestuffs are
obtained.

It is surprising that the process of the invention for preparing metal-containing

disazo dyestuffs of the above formula (1) can be carried out with such a good result, since it is known that the metal-free monoazo dyestuffs of formula (4) can only be coupled with diazotized aromatic amines in a strongly alkaline medium. Coupling in a strong alkaline medium is however impossible owing to the sensitivity of the groups of the formulae (2) and (3), which would become inactive.

In the metal-containing disazo dyestuffs obtained according to the present invention, the molar proportion of disazo dyestuff to metal is 1:1 in the case of copper complexes and 1:1 or 2:1 in the case of the metals cobalt or chromium.

The metal-containing disazo dyestuffs of the present invention are excellently suitable for the dyeing and printing of textile materials of natural or regenerated cellulose. For this purpose, they are applied to the said textiles according to the dyeing or printing methods usually employed for reactive dyestuffs and then fixed at ordinary or elevated temperature by treatment with an acid-binding agent; the latter may be applied either before, during or after application of the dyestuff.

The disazo dyestuff of the present invention yield on cellulose materials intense reddish blue to black shades which possess good to very good properties of wet fastness; especially fastness to washing. Moreover, the cotton dyeings possess a good to very good fastness to light, rubbing and dry cleaning.

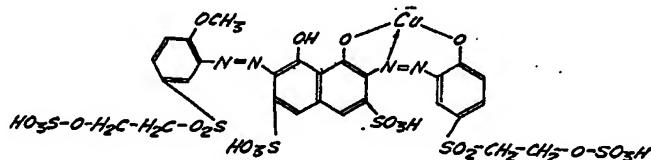
The following Example illustrate the invention.

EXAMPLE 1

a) 31.1 Parts by weight of 2-aminoanisole-4- β -hydroxyethylsulphone-sulphuric acid ester were dissolved in 250 parts by volume of water by the addition of 5.3 parts by weight of sodium carbonate. The solution was mixed with 100 parts by weight of semi-concentrated hydrochloric acid and diazotation was carried out at 0° C. with 20 parts by volume of a 5N sodium nitrite solution. 51.2 Parts by weight of 1,8-dihydroxynaphthalene-3,6-disulphonic acid (62.5%) were then added to the diazo suspension obtained and the pH-value of the reaction solution was adjusted to 4.5—5 by adding crystalline sodium acetate. Coupling was complete after a few hours. The red dyestuff formed was salted out by the addition of 40 parts by weight of sodium chloride, filtered and washed.

b) To effect coppering and demethylation, the wet filter cake was dissolved in 400 parts by volume of water at 60° C. and, after addition of 25 parts by weight of crystalline copper sulphate, the solution was stirred for 12 hours at a temperature in the range of from 85° to 90° C. The pH was maintained at 5 by adding sodium acetate. Then 80 parts by weight of sodium chloride were added, the precipitated violet complex copper dyestuff was filtered with suction and washed with 500 parts by weight of a 15% sodium chloride solution.

c) 31.1 Parts by weight of 2-aminoanisole-4- β -hydroxyethylsulphone-sulphuric acid ester were diazotized as described under a). The diazo suspension thus obtained was neutralized with crystalline sodium acetate and combined with a solution of the complex copper monoazo dyestuff obtained according to b) in 300 parts by volume of water. The pH-value of the mixture was maintained at about 6 during coupling by careful addition of sodium hydrogen carbonate. After 8—10 hours, coupling was complete. The dyestuff was salted out by the addition of 25% of sodium chloride (referred to the volume of the solution), filtered, washed with a 15% sodium chloride solution and dried at 50°—60° C. under reduced pressure. A blue black powder was obtained which dissolved in water to form a blue solution. The dyestuff, which corresponded to the formula



gave on cellulose fibres in the presence of sodium bicarbonate or sodium hydroxide navy blue prints or dyeings which had very good fastness to light and wet treatment.

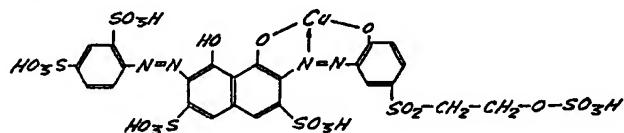
EXAMPLE 2

a) 29.7 Parts by weight of 2-aminophenol-4- β -hydroxyethylsulphone-sulphuric acid ester were dissolved in 500 parts by volume of water by the addition of 5.3

parts by weight of sodium carbonate and diazotized as described in Example 1, paragraph a). After neutralization of the diazo solution with sodium acetate, a solution of 51.2 parts by weight of 1,8-dihydroxynaphthalene-3,6-disulphonic acid (62.5%) in 500 parts by volume of water was added. The pH-value of the coupling solution was maintained at 5—5.5. A part of the red monoazo dyestuff formed precipitated during the coupling, which was complete after about 24 hours. Precipitation was completed by the addition of 100 parts by volume of sodium chloride. After having separated the dyestuff by filtration, it was washed with a dilute sodium chloride solution.

b) For preparing the complex copper monoazo dyestuff, the wet filter cake was dissolved in 1,000 parts by volume of water and mixed at room temperature with 25 parts by weight of crystalline copper sulphate. The solution was buffered with crystalline sodium acetate. After 5 hours, the formation of the complex was complete. 250 Parts by weight of sodium chloride were added to the solution, the precipitated dyestuff was filtered and washed several times with a 15% sodium chloride solution.

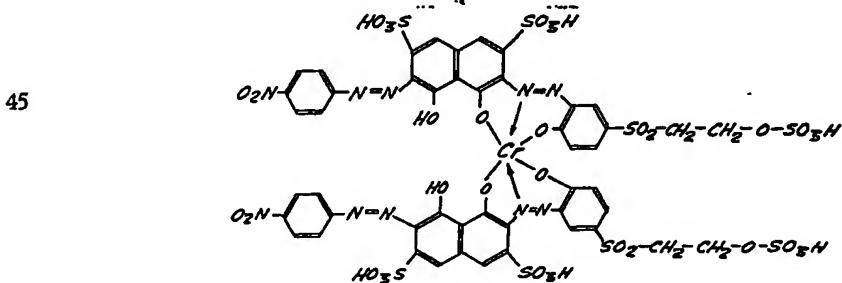
c) 25.3 Parts by weight of 1-aminobenzene-2,4-disulphonic acid were dissolved in 250 parts by volume of water and sodium carbonate until the solution showed a neutral reaction and, after addition of 100 parts by weight of semi-concentrated hydrochloric acid, was diazotized at 0° C. with 20 parts by volume of 5N sodium nitrite solution. The temperature of the diazo suspension was allowed to rise to about 20° C., the excess acid was neutralized with sodium acetate and then the diazo-component thus prepared was combined with a solution of the complex copper monoazo dyestuff obtained according to b) in 1,200 parts by volume of water. During coupling, the pH was maintained at 6—7 by careful addition of sodium carbonate. The dyestuff solution was then stirred over-night and the dyestuff was salted out by the addition of 180 parts by weight of potassium chloride and 180 parts by weight of sodium chloride, filtered and dried. The salt-containing dyestuff thus obtained which corresponded to the formula



dyed cellulose fibres in the presence of disodium phosphate and sodium hydroxide dark-blue shades which were fast to washing and to light.

EXAMPLE 3

The monoazo dyestuff obtained according to Example 2, paragraph a), was dissolved in 700 parts by volume of water. This solution was mixed with 60 parts by weight of chrome alum and adjusted to a pH-value of 5 by the addition of sodium acetate. The mixture was heated while stirring for 3 hours at 80° C. The blue solution of the 2:1-complex chromium dyestuff formed was then combined with a diazonium salt solution, which had been prepared by diazotizing 13.8 parts by weight of 4-nitro-1-aminobenzene in 250 parts by volume of water and 100 parts by weight of semi-concentrated hydrochloric acid with 20 parts by volume of 5N sodium nitrite solution and neutralization with crystalline sodium acetate. During coupling, a pH-value of 5 was maintained. The disazo dyestuff, which corresponded to the formula



was salted out with 250 parts by weight of sodium chloride, filtered, washed and dried.

The dyestuff gave on cellulose fibres in the presence of sodium hydroxide greenish grey to black dyeings which were fast to light and to washing.

5

EXAMPLES 4—28

The following Table lists further components from which metal-containing diazo dyestuffs may be obtained in a manner similar to that described in Examples 1 to 3, using 1,3-dihydroxynaphthalene-3,6-disulphonic acid as coupling component. Column (I) gives the diazo component (D) of the monoazo dyestuff, Column (III) gives the diazo component (A) of the diazo dyestuff, Column (II) the complex-bound metal atom and column (IV) the shades of the dyeings and prints on cotton.

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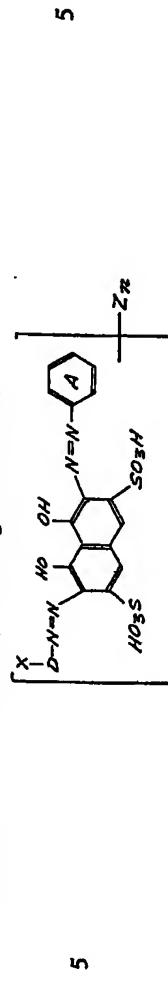
Example	1st Diazo component (I)	Complex bound metal (II)	2nd Diazo component (III)	Shade (IV)
4	2-aminophenol-4-β-hydroxyethyl-sulphone-sulphuric acid ester	Cu	1-aminobenzene-sulphonic acid	navy blue
5	"	Co	1-aminobenzene-4-sulphonic acid	grey to black
6	"	Co	1-aminobenzene-2,4-disulphonic acid	"
7	"	Co	4-nitro-1-aminobenzene	"
8	"	Cr	1-aminobenzene-4-β-hydroxyethyl-sulphone-sulphuric acid ester	"
9	"	Cr	2-aminoanisole-4-β-hydroxyethyl-sulphone sulphuric acid ester	"
10	2-aminophenol-5-sulphonic acid	Cr		navy blue

Example	1st Diazo component (I)	Complex bound metal (II)	2nd Diazo component (III)	Shade (IV)
11	2-aminophenol-5-sulphonic acid	Cr	2-aminoanisole-4- β -hydroxyethyl-sulphone-sulphuric acid ester	navy blue
12	2-aminophenol-4-sulphonic acid	Cu	1-aminoanisole-4- β -hydroxyethyl-sulphone-sulphuric acid ester	"
13	"	Cu	2-aminoanisole-4- β -hydroxyethyl-sulphone-sulphuric acid ester	"
14	2-amino-1-naphthol-5-sulphonic acid	Cr	1-aminoanisole-4- β -hydroxyethyl-sulphone-sulphuric acid ester	black
15	"	Cr	2-aminoanisole-4- β -hydroxyethyl-sulphone-sulphuric acid ester	navy blue
16	2-aminobenzene-1-carboxylic acid	Cr	1-aminoanisole-4- β -hydroxyethyl-sulphone-sulphuric acid ester	"
17	2-amino-4-chlorophenol	Cu	1-aminoanisole-4- β -hydroxyethyl-sulphone-sulphuric acid ester	"
18	2-amino-4-chlorophenol	Cr	1-aminoanisole-4- β -hydroxyethyl-sulphone-sulphuric acid ester	grey to black
19	2-amino-1-naphthol-4- β -disulphonic acid	Cr	"	navy blue
20	2-amino-4,6-dichlorophenol	Cr	"	grey blue
21	1-amino-2-methoxy-5-methylbenzene-4- β -hydroxyethylsulphonic acid ester	Cu	"	navy blue
22	"	Cu	2-aminoanisole-4- β -hydroxyethyl-sulphone-sulphuric acid ester	"
23	"	Cu	1-amino-2,5-dimethoxy-ethylene-4- β -hydroxy-ethylsulphone-sulphuric acid ester	"

Example	1st Diazo component (I)	Complex bound metal (II)	2nd Diazo component (III)	Shade (IV)
24	1-amino-2,5-dimethoxy-benzene-4-β-hydroxyethylsulphone-sulphuric acid ester	Cu	1-amino-2,4-dimethoxy-benzene-4-β-hydroxyethylsulphone-sulphuric acid ester	black
25	2-aminophenol-4-β-hydroxyethyl-sulphone-sulphuric acid ester	Cr	"	"
26	"	Cr	1-amino-2-methoxy-5-methyl-benzene-4-β-hydroxyethylsulphone-sulphuric acid ester	"
27	2-amino-1-hydroxy-4-vinyl-sulphonylbenzene	Cu	2-aminoanisole-4-β-hydroxyethyl-sulphone-sulphuric acid ester	navy blue

WHAT WE CLAIM IS:—

1. Complex copper, cobalt or chromium compounds of disazo dyestuffs which, in the form of their free acids, have the general formula

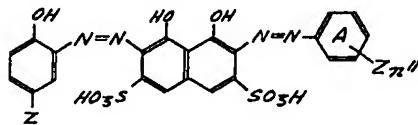


in which D represents the radical of a diazo component of the benzene or naphthalene series, X represents a hydroxyl or carboxyl group linked in *ortho*-position to the azo bridge, Z represents a group of the formula



which is linked to the residue D and/or residue A and n stands for 1 or 2 and in which the benzene nucleus A may be substituted.

2. Complex copper, cobalt or chromium compounds of disazo dyestuffs which, in the form of their free acids, have the general formula



in which Z and A have the meanings given in Claim 1 and n'' stands for 0 or 1.

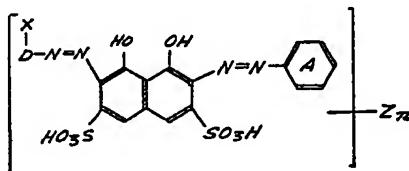
3. Any one of the complex metal-containing disazo dyestuffs obtainable as described in the Examples or with reference to the Table herein.

5 4. A dyeing or printing process, in which a dyestuff claimed in any one of Claims 1 to 3 is used.

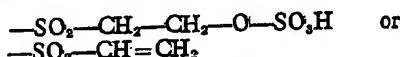
5 5. A dyeing or printing process as claimed in Claim 4 conducted substantially as described and exemplified herein.

10 6. Fibrous material, especially fibrous material of natural or regenerated cellulose, which has been dyed or printed by a process claimed in Claim 4 or 5.

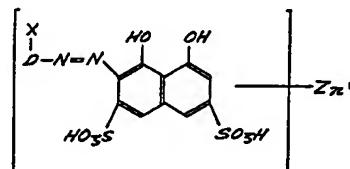
10 7. A process for the manufacture of complex copper, cobalt or chromium compounds of disazo dyestuffs, which in the form of the free acids, have the general formula



15 15 in which D represents the radical of a diazo component of the benzene or naphthalene series, X represents a hydroxyl or carboxyl group linked in *ortho*-position to the azo bridge, Z represents a group of the formula

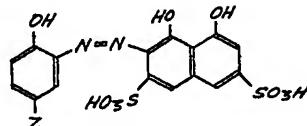


20 20 which is linked to the residue D and/or residue A and n stands for 1 or 2 and in which the benzene nucleus A may be substituted, wherein a complex copper, cobalt or chromium complex compound of a monoazo dyestuff, which in the form of its free acids, has the general formula



25 25 in which D, X and Z have the meanings given above and n' stands for 0, 1 or 2 is coupled with a diazotized amine of the benzene series in a weakly alkaline, neutral or weakly acidic medium, the components being so selected that the metalliferous disazo dyestuff obtained contains one or two groups of the formula Z.

30 30 8. A process as claimed in Claim 7, wherein the complex copper, cobalt or chromium compound of a monoazo dyestuff is used which, in the form of its free acid, corresponds to the formula



in which Z has the meaning defined in Claim 7.

35 35 9. A process as claimed in Claim 7 or 8 wherein the coupling takes place at 10° to 40° C. at a pH-value of from 4 to 9.

10. A process for the manufacture of complex copper, cobalt or chromium compounds of disazo dyestuffs as claimed in Claim 7 from any of the components specified herein substantially as described.

5 11. A process for the manufacture of complex metal disazo dyestuffs, conducted substantially as described in any one of the Examples or with reference to the Table herein. 5

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